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Biobased composite powders from PHA, waxes and lignocellulosic biomasses for powder-based additive manufacturing processes

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Abstract

Additive manufacturing (AM) is a method of production that greatly reduces the volume of waste material produced. The use of biobased materials that are sourced from biomass feedstocks (such as polyhydroxyalkanoates (PHA)) for AM applications is key to reducing our impact on the environment and contributing to a societal shift towards a circular bioeconomy. However, such materials are not easily employed with current AM technologies due to the technological limitations of the materials. Their mechanical properties are often poorer than those of petroleum-based materials, which limits their applications. Therefore, there is a need for new biobased composites with improved mechanical properties, which are also suitable for AM technologies. Formulating and/or reinforcing materials with different fillers, such as lignocellulosic powders, has been used to improve the mechanical properties of biobased materials. Among existing AM techniques, powdered additive manufacturing, such as selective laser sintering (SLS), has been widely developed due to many advantages: high accuracy and resolution, speed, reliability, and reduced dependency on support structures. In the present work, we have developed a new environmentally friendly process to prepare composite biobased powders from PHA, waxes and lignocellulosic filler suitable for SLS. The process, based on emulsification and dissolution/precipitation in eutectic solvents, appears to be non-specific and can be adapted to a wide range of PHAs, biobased waxes and lignocellulosic biomasses. Results have shown that the combination of such raw materials improves the properties of the composite powders for implementation in SLS applications.

Key words: Additive manufacturing, selective laser sintering, biobased materials, polyhydroxyalkanoates, waxes, processes, biocomposite powder

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1. Introduction

Additive manufacturing (AM) is a method of producing functional objects additively, layer by layer. This minimises the quantity of material required compared to subtractive techniques. The societal shift towards a circular bioeconomy drives efforts to combine additive manufacturing and environmentally sustainable materials. Nevertheless, implementation of such materials in AM technologies is still limited due to material properties compared to conventional polymers. The definition of “environmentally sustainable materials” is controversial and may only include one or more aspects among renewable-sourced, biodegradability, or environmental impact of the production process [1, 2]. Saidani et al. (2020), proposed to integrate the different aspects in a classification in which ranked a comprehensive range of biobased plastics based on the environmental impact of the production processes (CO₂ equivalent) and their biodegradability [2]. In particular, the PHAs (microbial polymers), appear to be promising materials as they have excellent biocompatible and biodegradable properties and a very low environmental impact [3]. However, their mechanical strength and hydrophilicity limit their applications [4] and numerous studies have explored formulations reinforced with different fillers such as lignocellulosic powders [5-8]. Most PHAs

also have low crystallisation rates, which complicates their use in traditional 3D printing processes.

Natural waxes (beeswaxes, or vegetable waxes) are also biocompatible and biodegradable, and exhibit hydrophobic and antibacterial properties [9]. Because of their low molecular weight and the lack of crosslinking in ester chains, waxes have weak mechanical properties, but it has been demonstrated that the addition of crystalline waxes favours the crystallisation process for low-density polyethylene [10] and reduces the setting time of hot melt adhesive [11, 12]. Waxes have been also used to tune the properties of PHA/wheat bran composite as a compatibiliser between the lignocellulosic filler and polymeric matrix [13].

Formulations from PHA, biobased waxes and lignocellulosic biomass can enhance the properties of each material and enable the design of biosourced, biodegradable, and biocompatible materials with improved mechanical, hydrophobicity and antibacterial properties, according to the formulation used. As an example: waxes will improve the properties of PHAs by adding hydrophobicity and antibacterial properties. They could also increase the crystallisation rate for some PHAs (e.g. mcl-PHA), enabling them to be implemented in additive manufacturing processes. For brittle polymers such as Polyhydroxybutyrate (PHB), waxes could introduce flexibility. The addition of PHAs to wax will enhance the mechanical properties of the wax while maintaining its biocompatibility and biodegradability. The addition of biobased filler as lignocellulosic powder to such matrices could also increase their crystallisation rate by initiating the nucleation process around biomass particles while additionally enhancing the mechanical properties of the composite. Therefore, composites combining wax, PHAs and lignocellulosic biomass powder could be suitable for a wide range of applications where biobased, biocompatible (depending on the type of filler) and biodegradable composite materials are required.

However, the rheological and mechanical properties of such composites make it challenging to produce filaments for FDM techniques [14]. Paste deposition processes [15] are possible, but the rheological properties of the formulations do not permit sufficient resolution for complex objects. Selective laser sintering (SLS) is instead a more promising AM technique for such materials. SLS is a powder bed fusion-based additive manufacturing technology that uses a laser system to form objects by sintering powdered materials layer by layer. SLS has many advantages: high accuracy, speed, reliability and lack of support structures, and it is a robust commercial AM technology. Traditionally SLS is used for the additive manufacturing of metals, and currently, the range of commercially available powdered polymer materials that can be used in the process is limited. Polyamide (PA) is the most widely used commercial material [16]. Over the past two years, there has been increasing interest in the development of new biodegradable and biobased polymer and composite powders, with potential applications in advanced fields such as pharmaceuticals and tissue engineering [16-18] for which a formulation from PHA/Waxes/biobased filler would be attractive.

The quality of 3D printed objects produced using SLS is directly related to the microstructure of the powder bed depending of intrinsic and bulk properties of the powders [16, 19-21]. The particle size distribution of the powder, in particular the median particle size and dispersion of the distribution, is crucial as it directly influences the spreadability of the powder in the SLS device, the printing accuracy and the porosity of the 3D printed object. Obtaining fine and easily spreadable biobased composite powders is challenging. Typically, when printing such polymers by SLS, blends of powders from different materials are used [22, 23], but composite particles are better suited to the selective laser sintering process as it avoids segregation between the different compounds of the blend and enables better interaction between filler and matrix. Milling of composites obtained from compounding will generate a broad particle size dispersion that will reduce the spreadability of the powder for the SLS process and are not suited to matrices such as PHA/PHB or wax, which have low glass

transition and melting temperatures. In a green process vision, the ideal situation for an AM process would be to use the PHA in the microsphere shape directly, as produced within the microorganism, instead milling PHA granules to obtain a fine powder.

This work focuses on the development of a new and sustainable process to produce composite particles for SLS printing consisting of a combination of PHA, biobased waxes and lignocellulosic powder as a filler. A literature review enabled us to screen (a) the different processes that can be used to produce such powders and (b) adaptations that should be done to make them more suitable. Based on this study, two processes have been proposed, and their potential to generate particles suitable for SLS printing was evaluated by the particle size distributions in comparison to those of PA12, a standard polymer powder for SLS printing

2. State of the art: Production of composite powder from wax and polymer

Melt emulsification processes have been previously used to prepare solid wax particles. In melt emulsification, the dispersed phase is heated above its solidification temperature in a continuous phase with emulsifiers (surfactants), and a device providing high shear and elongational stress is used to form the emulsion. It is rapidly cooled by adding cold water to solidify the droplets, and a suspension of spherical particles is obtained [24]. Solid particles can be used as surfactant to stabilise the emulsion (i.e. Pickering emulsion) [25]. Composite wax particles prepared by emulsification from petroleum-based waxes have been reported [26, 27]. With water as the emulsion solvent, this process could be extended to other polymers with melting points below 90°C.

For polymers with higher melting points, the use of dissolution-precipitation [18] or thermally induced phase separation processes (TIPS) [16] have been proposed to produce spherical particles suitable for SLS applications. These processes have been used to produce PA12/CF (polyamide 12/carbon fibre), neat PEEK (poly ether ether ketone) and PEEK/CNT (carbon nanotubes) composite powders. In the dissolution-precipitation process, polymer is dissolved in a suitable solvent and filler is added to form a homogeneous suspension. The suspension is then gradually cooled to ambient temperature. The polymer crystallises, taking the filler as heterogeneous nuclei. Finally, the composite powder is recovered after distilling out the solvent, vacuum drying and milling. In the TIPS process, polymer is dissolved in a solvent at elevated temperature followed by liquid-liquid phase separation (LLPS), droplet nucleation, growth and precipitation during the subsequent cooling stage. In both cases, the solvents used are not green and the process requires steps for solvent recycling.

In recent years, Deep Eutectic Solvent (DES) appears to be a cheap and sustainable alternative to traditional solvents, particularly with respect for synthesis media [28]. DES is a type of ionic solvent composed of a mixture that forms a eutectic with a melting point much lower than either of the individual components. Most common DES are based on choline chloride (Ch-Cl), carboxylic acids, and other hydrogen-bond donors, e.g., urea, citric acid, succinic acid and glycerol. Different molecules can also be combined to produce natural deep eutectic solvents [29]. Reline, an eutectic mixture of choline chloride and urea in a 1:2 molar ratio, is a well-known DES, (Ch-Cl-Ur) [30]. The use of DES in polymer chemistry is still emerging but it can lead to many developments, from polymer dissolution to changes in polymer properties [31].

Melt emulsification and dissolution/precipitation in eutectic solvents has been selected and tested in different formulations to cover the whole range of PHA, and ensure the non-specificity of the processes.

3. Materials and Methods

3.1 Raw materials preparation

The raw materials included in the formulations tested were purchased/prepared as described below. The particle sizes and melting temperatures of the raw materials are reported in Table 1. Particle size distribution was measured by laser diffraction according to the protocol in section 3.5: Particle size analysis. Melting temperatures are provided in supplier datasheets (for the materials abbreviated PHB, WAX) or measured experimentally by measuring the temperature of the solid/liquid transition (for the material abbreviated mcl-PHA).

Wax: Refined yellow beeswax pellets were purchased from NZ Beeswax Ltds. This will be referred to as beeswax in the remainder of the document, and abbreviated as BW

PHA: To cover a range of melting temperatures, two different types of PHA were used: A fine powder of Poly[(R)-3-hydroxybutyric acid] (abbreviated PHB) purchased from Sigma-Aldrich (product 363502), and a medium-chain-length-Poly(3-hydroxyalkanoate) (abbreviated mcl-PHA) (abbreviated mcl-PHA) produced according to the procedure described by Collet et al.[32]

Purification of PHA: Cells were resuspended to 400 g/L in a homogenisation buffer containing: 10 mM Tris pH 7.5, 2 mM EDTA. SDS was added to 5% and cells were stirred to resuspend, before passing 3 times through a microfluidics homogeniser M-110P at maximum pressure (30,000 psi), cooled with ice. Ethanol was then added to 20% final concentration and the suspension was centrifuged (20,000g, 1h, 10 C). After discarding the supernatant, the pellets were resuspended in an equal volume of buffer (10 mM of Tris at pH 7.5, 2 mM of EDTA and 20% of ethanol). This washing/centrifugation process was repeated twice, with resuspension in half the volume of buffer (10 mM Tris pH 7.5, 2 mM EDTA, 20% Ethanol)

Lignocellulosic filler: The lignocellulosic powders used in this study are maritime pine bark (*Pinus pinaster*) purchased from a local store (Botanic, Montpellier, France) and finely milled in three steps (coarse, intermediate and fine milling with vibratory ball mill according to the procedure described by Rajaonarivony et al. [33]. This powder is named pine bark powder (abbreviated PB) in the remainder of the document.

Choline-Chloride-Urea solvent: was prepared from choline chloride purchased from Sigma Aldrich (CAS Number 67-48-1) and urea purchased from Merck (CAS number 57-13-6) in the molar ratio 1:2. Before mixing, both compounds were oven-dried at 55°C for 12 hours [34]. The dried powders were then mixed at 80°C until completely melted to produce the solvent, which was stored in an oven at 55°C to prevent water uptake. The solvent is named Ch-Cl-Ur.

Table 1 : Main characteristics of the raw materials involved in the different formulations.

	Particle size characteristics				Melting temperature
	D ₁₀	D ₅₀	D ₉₀	SPAN	
mcl-PHA	0.689	1.197	3.451	2.306	48.4 °C
PHB	3.9565	26.8135	74.827	2.643	172 °C
BW	Pellets (length: 2-4 cm, diameter 0.5 – 1cm)				55 °C
PB	3.346	21.427	78.441	3.505	

3.2 Formulations:

Eight formulations were selected to screen a range of ratios and the potential of both processes in a limited number of trials (see Table 2). Each raw material used in the formulation was tested alone and in combination. When lignocellulosic biomass was added as a filler, the mass proportion of the matrix (PHA, wax or PHA+wax) and those of the fillers were 60wt.% and 40wt.%, respectively.

Table 2 : The different formulations per weight fraction

N°	Formulations	mcl-PHA	PHB	BW	PB
1	mcl-PHA-PB	60%	-	-	40%
2	mcl-PHA -BW-PB	20%	-	40%	40%
3	BW	-	-	100%	-
4	BW-PB	-	-	60%	40%
5	PHB	-	100%	-	-
6	PHB-BW	-	50%	50%	-
7	PHB-PB	-	60%	-	40%
8	PHB-BW-PB	-	30%	30%	40%

3.3 Melt emulsification process

This process was applied to formulations 1 to 4. The matrix (mcl-PHA, or/and beeswax) and lignocellulosic powder were melted in a beaker on a hot plate and mixed by magnetic stirring or homogenisation. Hot water (90°C) was then added to the mixture to create an oil-in-water emulsion. Different ratios o/w (oil in water) between 0.1 and 0.25 v/v (in volume) were tested in preliminary work and a ratio of 0.2 was selected for the results presented here as it leads to the more homogeneous emulsion.

The mixture was maintained at 90°C and continuously homogenised for 5 minutes using a rotor/stator device (Ultra-Turrax T 25 disperser IKA® T25) operating at 12,500 rpm. Then, while maintaining the homogenisation, the emulsion was rapidly cooled by direct addition of ice until it dropped to a temperature below 20°C. This led to solidification of the droplets into particles, that were then separated from the liquid phase by filtration.

3.4 Dissolution and precipitation in Choline-Chloride

The different compounds (Wax, PHB and Pine bark powders) were first dissolved and/or melted in Ch-Cl-Ur for 12 hours at 80°C. Then, water (2°C) was added. The simultaneous modification of the temperature and the ionic balance of the solution lead to the generation of particles. As the use of Ch-Cl-Ur to dissolve PHA and melt waxes has not yet been studied, two sets of experiments were carried out to understand the solubility of each compound of the matrix and their miscibility.

Set 1: For formulations 3 to 8, 500 mg of the raw materials were melted or dissolved in 15 ml of Ch-Cl-Ur for 12 hours at 80°C in the ratio reported in Table 2. Subsequently 2 ml of the solution was taken and 10 ml of water (2°C) was added with stirring to precipitate the composite particles. The temperature of the final mixtures (including water) was below 12°C. Two controls were carried out with pure Ch-Cl-Ur and Pure Pine bark powder (500 mg). In the first case, no precipitation was observed, and in the second case, the particle size distribution after 12 hours at 80 °C was similar to that of the raw powder, suggesting no significant dissolution of pine bark powder in the solvent.

Set 2: To study the effect of dissolving/melting PHB and beeswax, two additional experiments were carried out as described below:

- 1 ml of the solution containing only PHB (Formulation 5. PHB) and 1 ml of the solution containing only the beeswax (Formulation 3. BW) were mixed just before the addition of 10 ml of cold water to generate composite particles (Formulation 6. PHB-BW)
- 0.6 ml of the solution containing only PHB (Formulation 5. PHB), 0.6 ml of the solution containing only the beeswax (Formulation 3. BW) and 0.8 ml of the control solution with only pine bark powder were mixed just before the addition of 10 ml of cold water to generate composite particles (Formulation 8. PHB-BW-PB)

3.5 Particle analysis:

Microscopy: The images were captured using a Leica M125C stereomicroscope and analysed using ImageJ software

Particle size analysis: The particle size distributions of the composite powders were measured by laser diffraction using a Mastersizer 2000 (Malvern, UK) equipped with a Hydro2000S system. Data was processed using the Fraunhofer method. Particle size distribution was recorded and main indicators, d_{10} , d_{50} , d_{90} , SPAN and specific surface area, were extracted from the distribution. Measurements were carried out in triplicate and average particle size distribution was calculated.

4. Results and discussion

4.1 Melt emulsification process

Obtaining satisfactory melt emulsion required high shear mixing. The quick addition of ice was successful in generating particles. In the case of particles including the lignocellulosic biomass as a filler (1.ME-mlc-PHA-PB, 2.ME-mlc-PHA-BW-PB, 4. ME-BW-PB) a rapid sedimentation of particles that were easily separated from the solvent by filtration was observed in the beaker. Sedimentation was not observed for Formulation 3. ME-BW due to a greater proportion of smaller particles, as illustrated in Table 3, summarising the main indicators of the particle size distribution ($d_{50} = 1.8 \mu\text{m}$).

Table 3 : Main particle size indicators of the different formulations

	Formulation	D10 μm	D50 μm	D90 μm	Span	Specific surface area ($\text{m}^2.\text{g}^{-1}$)
	SLS reference powder					
	PA12	35.4	55.9	85.5	0.89	0.13
	Melt emulsification Processes (ME)					
	1. ME-mlc-PHA-PB	16.3	47.5	99.6	1.75	0.29
	2. ME-mlc-PHA-BW-PB	19.7	53.6	122	1.92	0.26
	3. ME-BW	0.8	1.8	43.4	24.2	3.61
	4. ME-BW-PB	22.5	72.5	145	1.69	0.21
	Dissolution/Precipitation in Choline-Chloride (DP)					
Set 1	3. DP-BW	1.61	7.55	32.5	3.91	1.34
	4. DP-BW-PB	22.2	54.7	102	1.46	0.25
	5. DP-PHB	1.64	6.40	32.3	4.77	1.63
	6. DP-PHB-BW	4.26	34.8	110	3.03	0.59
	7. DP-PHB-PB	2.64	12.7	47.5	3.55	0.99
Set 2	8. DP-PHB-BW-PB	7.35	78.8	327	4.04	0.37
	6. DP-PHB-BW	2.36	14.5	54.5	3.59	2.36
	8. DP-PHB-BW-PB	2.25	11.6	51.1	4.20	1.06

Microscopic observations (Figure 1) of the coarser particles of this formulation revealed spherical particles. The more angular appearance of composite particles from BW-PB may be related to the coating of the beeswax bubbles by the pine bark particles creating a Pickering emulsion and favouring the generation of larger particles.

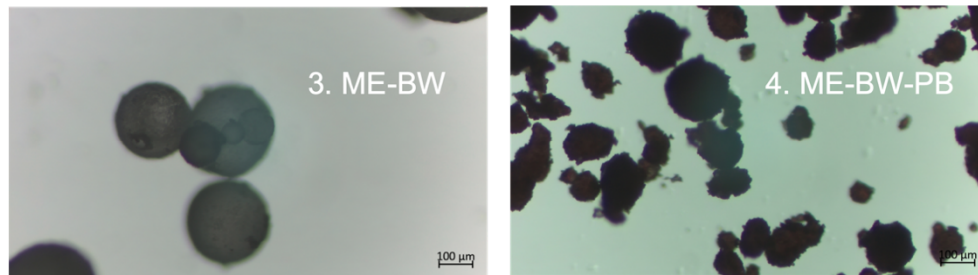


Figure 1: Microscopic observations of particles generated by melt emulsification processes for Formulations 3. ME-BW (pure Beeswax) and 4. ME-BW-PB

Note that in the case of the three-components formulations that include pine bark powder as a filler, the median particle sizes were very close to those of PA12 (see Table 3). The value of SPAN, highlighting the scattering of the distribution is slightly broader than those of PA12 in relation to the lower and higher value of the 10th (d_{10}) and the 90th (d_{90}) percentiles of the distribution (giving an indication of the size of the smaller and larger particles). However, all the d_{90} values are below 150 μm and are still within the range of other commercial powders used in SLS processes [35].

4.2 Dissolution and precipitation in choline-chloride

Visual observations of Formulation 5.DP-PHB after dissolution did not detect any remaining particles, and the particle size indicators after the precipitation step (Table 3) are very different from those of raw PHB (Table 1), showing a successful dissolution of the polymer and then precipitation of the PHB in particles of smaller size. The span of the particle size distributions are larger than those of PA12, however higher shear stirring system should result in more homogenous particle size distributions. The powder generated from the formulation with pure compounds (3. DP-BW, 5. DP-PHB) has a median particle size smaller than 10 μm that can lead to spreadability issues, prior to the printing process, or during the printing process itself. For all the other formulations, the median particle sizes are typically in a range comparable to the commercial powder used for SLS printing. However, the D_{90} for Formulation 8. DP-PHB-BW-PB (Set 1) is higher than 200 μm and so less suitable for SLS printing [36].

For Formulations 6. DP-PHB-BW and 8. DP-PHB-BW-PB the difference between the experiments carried out in Set 1 and Set 2 is due to the time in which the different components are in contact at 80°C before precipitation (12 hours in case of Set 1) and only few minutes for the experiments (Set 2). The high differences observed for the main indicators of the particle size distribution suggest stronger interactions between the compounds in the case of the Set 1. These interactions could be due to polymer and wax interaction in the presence of Ch-Cl-Ur during the dissolution time. DES has been reported to induce structural change in the polymer structure [31]. Interestingly the observations of the particle size distributions (not presented here) for Formulations 3. DP-BW, 5. DP-PHB and 6. DP-PHB-BW show that the beeswax drives the formation of the particles in Formulation 6. DP-PHB-BW as this particle size distribution is closer to that of 3. DP-BW than that of 5. DP-PHB.

4.3 Composite characters of the powder

To confirm the composite character of the powder, i.e: 3 compounds imbedding in the particles, particle size distributions of powders precipitated separately (3-DP-BW, 5DP-PHB and pine bark powder) have been compared to those mixed after precipitation (8-PHB-BW-PB-blend) and to those of Formulation 8. DP-PHB-BW-PB Sets 1 and 2 (Figure 2).

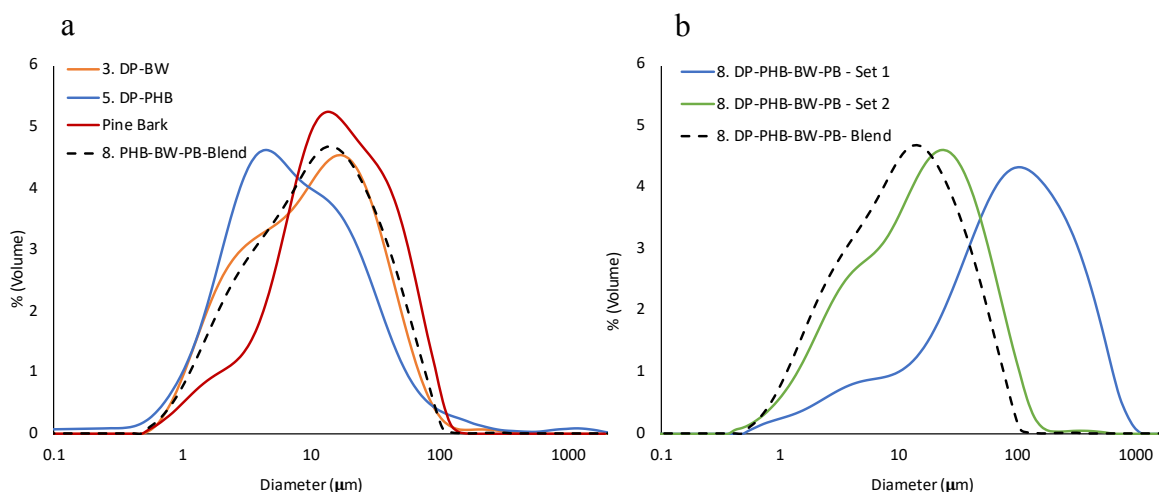


Figure 2: Particle size distribution of pure compound and of a blend of 3 compounds precipitated separately and mixed in the same ratio as Formulation 8. PHB-BW-PB (a). Particle size distribution of Formulation 8. DP-BW-PW obtained according to the protocols for Set 1, Set 2, and mixed after precipitation.

In Figure 2a the particle size distribution of 8. PHB-BW-PB-blend is typically the mathematical sum of the particle size distribution of each powder alone. Contrarily, the particle size distributions of 8. DP-PHB-BW-PB Set 1 and Set 2 are shifting through coarser particles and this is very significant for 8. DP-PHB-BW-PB where the compounds remain a long time in contact before precipitation. This suggests that in the case of 8. DP PHB-BW-PB Sets 1 and 2, the particles are made of several compounds, and the contact time prior to the precipitation is crucial for managing the size and the properties of the composite particles. Further chemical analysis is planned in the coming months to investigate the nature of these interactions during the melting step, and their impact on the particles and powder properties in view of process optimisation.

5. Conclusion

We have demonstrated proof-of-concept processes enabling the production of composite biobased particles from biobased wax, lignocellulosic filler and a wide range of PHA. Two potential pathways are described: melt emulsification and dissolution/precipitation in a deep eutectic solvent. The size of the particles obtained is in the range of those targeted for powdered 3D printing, especially SLS printing. Preliminary printing tests have demonstrated the potential of such powders that could be used in technical applications. However, the process conditions significantly influence the size of the particles and the time in which the different compounds are in contact before the generation of the solid particles. It is anticipated that this is a result of strong interactions between the compounds which are present during the dissolution phase, in the case of dissolution/precipitation in deep eutectic solvent. The next step will be the optimisation of the process and the regulation of the particle properties.

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